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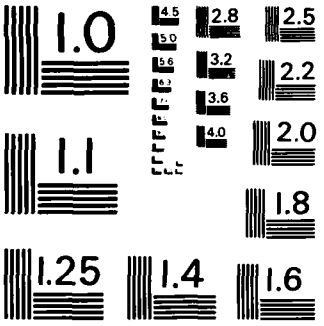

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Photoluminescent Response of Palladium-Cadmium Sulfide and Palladium-Graded Cadmium Sulfoselenide Schottky Diodes to Molecular Hydrogen

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The bulk photoluminescence (PL) of Schottky diodes constructed from Pd and n-type CdS (Pd-CdS) and from n-type, graded CdS_xSe_{1-x} ($0 \leq x \leq 1$; x = 1 at surface) (Pd-CdS_xSe_{1-x}) is sensitive to molecular H_2. For the Pd-CdS diode, exposure to H_2 (3:1, N_2:H_2 mixture) significantly enhances the PL intensity of edge emission (λ_{max} ~510 nm) relative to the intensity in air; using a dead-layer model, the corresponding reductions in depletion width and Schottky barrier height can be estimated. For the Pd-CdS_xSe_{1-x} diode, H_2 changes the

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spectral distribution; PL from this material, color-coded to spatially resolve e^-h^+ pair recombination, indicates the depth over which the electric field is reduced in the semiconductor. These phenomena demonstrate optically-coupled chemical sensing of hydrogen.

INTRODUCTION

The bulk photoluminescence (PL) of semiconductors has proven to be a useful probe of Schottky barrier characteristics in both semiconductor/metal diodes[1] and photoelectrochemical cells (PEC's).[2] In particular, the electric field in the semiconductor can be estimated from PL intensity using a dead-layer model: Electron-hole (e^--h^+) pairs formed within a distance from the interface on the order of the depletion width do not contribute to PL. While the importance of surface properties on bulk PL has been described[3,4], their interrelationship has not been examined experimentally in detail.

In choosing a system for such studies, our interest was drawn to Schottky diodes constructed with Pd because of the known sensitivity of their current-voltage (i-V) properties to gaseous H_2.[5-8] In general, Schottky barriers resulting from junctions of Pd with a variety of n-type semiconductors decreased upon exposure of the diode to H_2, reflecting diminution of the Pd work function by the gas.[9] The effect is sufficiently sensitive to H_2 concentration that Pd-CdS[5] and Pd-TiO_2[6] Schottky diodes have been proposed as H_2 detectors. Variation in Schottky barrier height with H_2 appears to also strongly influence the efficiency with which metal-coated semiconductor electrodes evolve H_2 in PEC's.[10]

We report herein that PL intensity from Pd-CdS Schottky diodes is substantially perturbed by exposure of the diode to H_2. Moreover, the PL properties are consistent with a dead-layer model, allowing calculation of the variation in electric field thickness with exposure to H_2. Schottky diodes constructed from Pd and a graded CdS_xSe_{1-x} ($0 \leq x \leq 1$; $x=1$ at surface) semiconductor[11,12] (Pd-CdS_xSe_{1-x}) evince a change in spectral distribution upon exposure to H_2; the color-coded nature of the light emitted from this semiconductor can be used to map the effective electric field in this solid and its perturbation by H_2. Besides illustrating the coupling of surface interactions to bulk PL, these studies demonstrate the feasibility of constructing optically-coupled chemical sensors.

EXPERIMENTAL SECTION

Samples of n-type, single-crystal, CdS and CdSe c-plates (1-mm thickness; ∿2 ohm-cm resistivity) were purchased from Cleveland Crystals, Inc. and cut into pieces of ∿0.25-cm^2 area. Graded samples of n-CdS_xSe_{1-x} ($0 \leq x \leq 1$) where the graded zone had a thickness of ∿1.0 μm were prepared by vapor-phase diffusion of S into CdSe and characterized as described previously.[12] Prior to Pd deposition on its 0001 Cd-rich face, CdS was etched in Br_2/MeOH (1:10 v/v); the graded CdS_xSe_{1-x} samples were not etched owing to the thinness of the graded layer.

Deposition utilized Pd foil (50x50x0.1 mm; >99.997% metallic purity; Aesar Co., Seabrook, NH) and a SPI Super Sputter apparatus. Sputtering was conducted at $2x10^{-4}$ torr Ar pressure and 60-μA beam current for ∿45 s; a parallel deposition onto Pt foil was used in conjunction with electrochemical stripping (0.75 V vs. SCE in 1M HCl aqueous electrolyte) to estimate the Pd layer thickness to be ∿100 Å. After deposition, electrical contact was made to the translucent Pd layer with Ag epoxy and to the back surface with Ga/In eutectic and Ag epoxy; Cu wires were connected to the Ag epoxy and current-voltage properties obtained with a PAR Model 173 potentiostat and Model 175 programmer.

PL spectra were recorded using 457.9- and 488.0-nm excitation from a CR-12 Ar^+ laser and an Aminco-Bowman spectrometer equipped with a Hamamatsu R446S PMT. The sample was enclosed in a cell which permitted dry N_2, a 3:1 N_2:H_2 mixture (Air Products tank of H_2 mixed with in-house N_2), or air to bathe the sample; flow rates of ∿0.5 ℓ/min were employed. Optical properties of the Pd film were examined by depositing the metal on a microscope slide; transmission and reflectivity of 457.9-, 488.0-, and 514.5-nm light were measured in air and the N_2/H_2 medium.

The PL spectrum from a Pd-CdS sample in air, illuminated through the metal with 457.9-nm ultraband gap (Eg ∿2.4 eV) light, is characterized by band edge emission at ∿510 nm,[13] as shown in Fig. 1. When a 3:1 mixture of N_2:H_2 is passed over the sample, Figure 1 reveals that the PL intensity is enhanced by approximately 70%; the enhancement occurs over ∿30 s with the ∿100-Å-thick Pd layer. PL enhancement requires the presence of Pd but does not appear to derive from changes in the metal's optical properties: optical transmission and reflectivity of the metal film, deposited on a microscope slide, were insensitive to the presence of H_2. After flushing the sample cell with N_2 and then with air, the PL intensity returns to its original value. This effect is reversible over at least 10 cycles. If more penetrating 488.0-nm light is used for excitation, the PL intensity is augmented by ∿40% with exposure to H_2. From current-voltage data, the Pd-CdS structure exhibits typical diode behavior in air and in the N_2/H_2 medium.

These spectral changes are consistent with a reduction in Schottky barrier height resulting from the dissolution of H_2 in Pd, a well-studied phenomenon.[5-10] Qualitatively, the PL intensity is expected to rise because the smaller electric field in the semiconductor allows a larger fraction of e^--h^+ pairs to radiatively recombine. By regarding the region supporting the electric field as being completely nonemissive, i.e., a dead layer, a quantitative expression for relative PL intensity can be obtained, eq. (1); this treatment assumes that the CdS surface recombination velocity in the diode is either very large or insensitive to H_2.[2,3] In eq. (1), ϕ_{H_2} and ϕ_{air} are the radiative quantum yields in H_2 and

$$\frac{\phi_{air}}{\phi_{H_2}} = \exp(-\alpha'\Delta D) \qquad (1)$$

in air; ΔD is the difference in dead-layer thickness between the two media; and $\alpha' = (\alpha+\beta)$ with α and β the solid's absorptivities for the exciting and emitted light, respectively. For CdS, α for $E \perp c$ polarized light is 6×10^4 and $\sim(9\text{-}10)\times10^4$ cm^{-1} for 488.0- and 457.9-nm light, respectively; β is 7×10^3 cm^{-1} at 510 nm.[14]

The PL enhancements seen for the two excitation wavelengths employed give a consistent value for ΔD of $\sim$500-600 Å. This value for the contraction of the electric field upon exposure to H_2 can be used to calculate a reduction in Schottky barrier height of the initial height is known. Literature estimates for the Pd-CdS barrier height in air range from $\sim$0.5-0.8 eV;[5,7] our i-V curves yield an estimated height of 0.6 eV. The depletion width W is related to barrier height qV by eq. (2), where ε_o is the permittivity of free space, q is the electronic

$$W = \sqrt{\frac{2\varepsilon\varepsilon_o V}{q\ N_D}} \qquad (2)$$

charge, and ε and N_D are the semiconductor's dielectric constant and charge carrier density; for our samples, ε and N_D are $\sim$10 and 9×10^{15} cm^{-3}, respectively.[15] Substitution into eq. (2), equating D with W, leads to an estimated decline in barrier height of 0.2 eV. Literature values vary from $\sim$0.5 eV[5] to $\sim$0.2 eV (extrapolated).[7] The range of values likely reflects variations in sample preparation.[16]

A complementary system with H_2-sensitive PL is the Pd-CdS_xSe_{1-x} Schottky diode. The PL spectrum in air is shown in Fig. 2 and consists of edge emission from all of the CdS_xSe_{1-x} compositions which comprise the $\sim$1.0-μm-thick graded zone, from CdS at the surface to the CdSe (E_g $\sim$1.7 eV; λ_{max} $\sim$720 nm) substrate.[12] A linear correlation exists between composition x and the emission band maximum, eq. (3).[13] In conjunction with AES/Ar^+ sputter etch data, eq. (3) provides

$$\lambda_{max}(nm) = 718 - 210\,x \qquad (3)$$

a map of radiative recombination in the solid: The PL is color-coded to indicate the depth from the surface at which e^--h^+ pair recombination occurs. Perturbation of PL by applied potential reflects changes in the effective electric field

(EEF) in the solid[11,12]; we use the term "EEF" to reflect the fact that the electric field of this solid is complex and contains contributions, e.g., from band-edge gradients, in addition to the field arising from the Schottky barrier.

Exposure of a Pd-CdS_xSe_{1-x} diode to H_2 results in asymmetric enhancement of as much as 50% in the blue end of the PL spectrum, Fig. 2; the effect corresponds to a modest color change. The material has diode i-V characteristics in both environments. Qualitatively, the PL enhancement at shorter wavelengths indicates a reduction in the EEF in the near-surface region of the semiconductor, since it is the near-surface, S-rich compositions which give rise to the emission. A more quantitative estimate of the affected region is afforded by the cessation of spectral changes for $\lambda \gtrsim 600$ nm. From eq. (3) and AES/Ar^+ sputter etch data, exposure to H_2 influences the EEF to a depth of $\sim$0.1 μm (1000 Å) from the surface.

In summary, bulk PL from Pd-CdS and Pd-CdS_xSe_{1-x} Schottky diodes provides a sensitive probe of changes in the electric field of the semiconductors resulting from a surface interaction with H_2. The ability to transform molecular surface interactions into a change in bulk PL intensity (Pd-CdS) or color (Pd-CdS_xSe_{1-x}) could have applications to the design of optically-coupled chemical sensors. Further experiments designed to couple analyte sensitivity to PL are underway in our laboratories.

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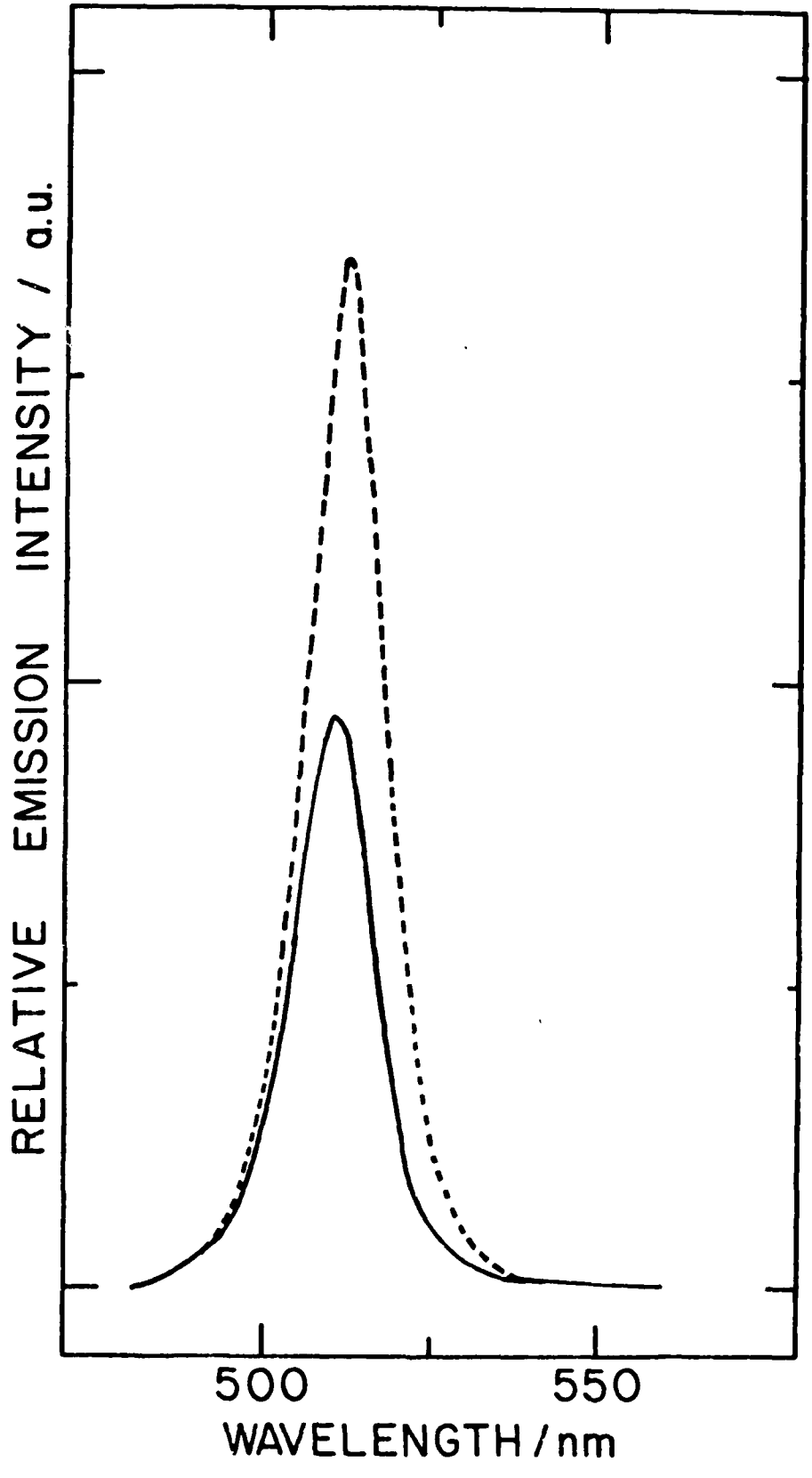
Figure Captions

Figure 1. Uncorrected PL spectra of a Pd-CdS Schottky diode in air (solid line) and in a 3:1, N_2:H_2 atmosphere (dashed line). The sample was excited with the same intensity ($\sim$40 mW/cm^2) of 457.9-nm light in both experiments, using an identical sample-detection optics geometry.

Figure 2. Uncorrected PL spectra of a Pd-CdS_xSe_{1-x} Schottky diode in air (solid line) and in a 3:1, N_2:H_2 atmosphere (dashed line). The sample was excited with the same intensity ($\sim$40 mW/cm^2) of 457.9-nm light in both experiments, using an identical sample-detection optics geometry.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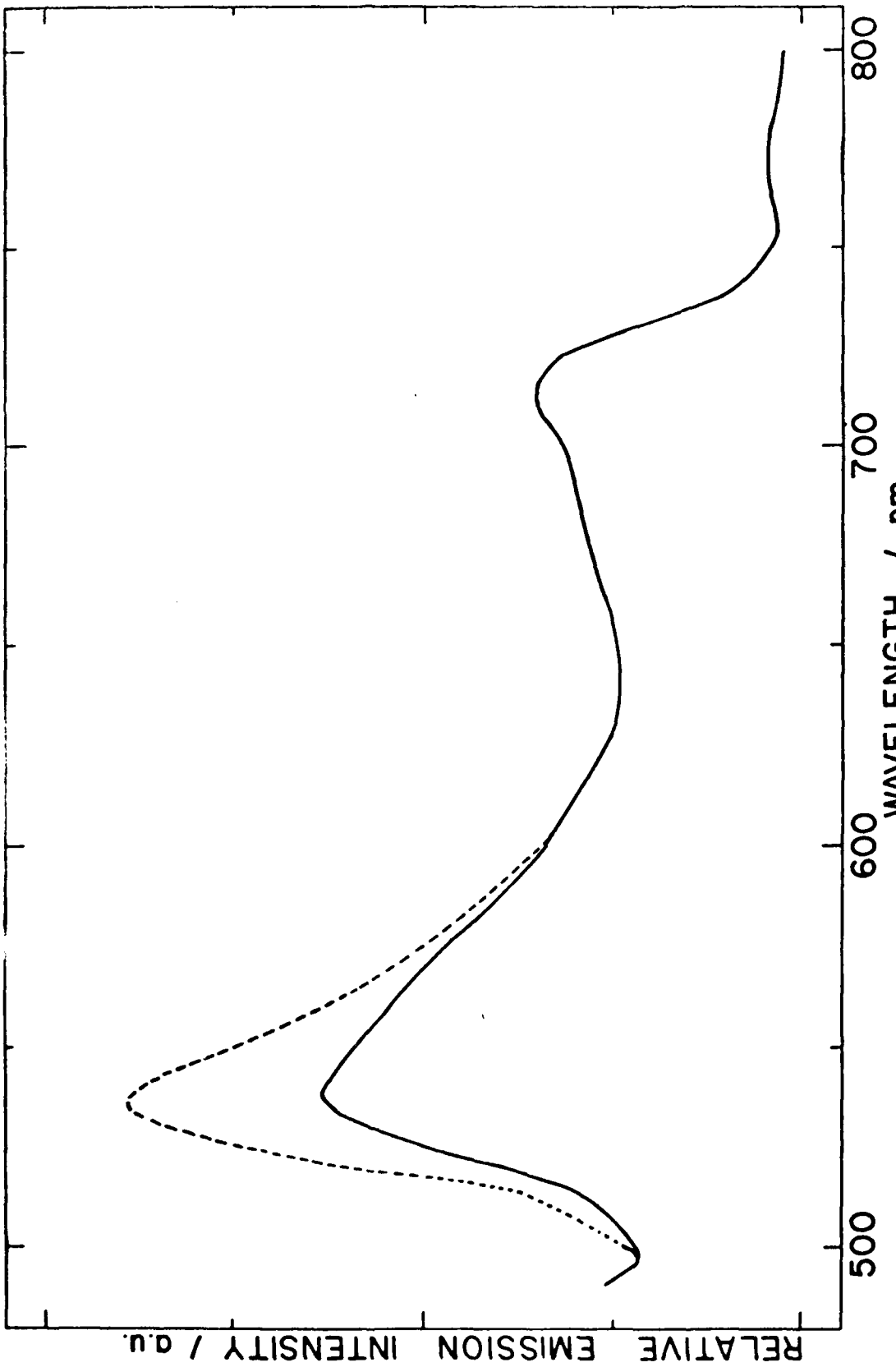
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